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(54) **Hydrochlorofluorocarbon azeotropic or azeotropic-like mixture.**

(57) A hydrochlorofluorocarbon azeotropic or azeotropic-like mixture comprising at least one member selected from the group consisting of hydrogen-containing fluoropropanes of the formula I:

$CH_aCl_bF_cCF_2CH_xCl_yF_z$ (I)

wherein $a+b+c=3$, $x+y+z=3$, $a+x\geq 1$, $b+y\geq 1$, and $0\leq a,b,c,x,y,z\leq 3$, and at least one member selected from the group of compounds II consisting of halogenated hydrocarbons having a boiling point of from 20 to 85°C other than said hydrochlorofluoropropanes, hydrocarbons having a boiling point of from 20 to 85°C and alcohols having from 1 to 4 carbon atoms.

HYDROCHLOROFLUOROCARBON AZEOTROPIC OR AZEOTROPIC-LIKE MIXTURE

The present invention relates to a novel hydrochlorofluorocarbon azeotropic or azeotropic-like mixture which can be used as a chlorofluorocarbon alternative and which has excellent properties as a solvent and so on.

Chlorofluorocarbon compounds (hereinafter referred simply as CFCs) have little toxicity and are, in many cases, non-flammable and chemically stable. Various CFCs having different boiling points are available. By virtue of such properties, 1,1,2-trichloro-1,2,2-trifluoroethane (R113) is used as a solvent or a blowing agent; trichloromonofluoromethane (R11) is used as a blowing agent or a propellant; and dichlorodifluoromethane (R12) is used as a propellant or a refrigerant.

Chemically stable R11, R12 and R113 have long lifetime in the troposphere and reach the stratosphere, where they will be dissociated by solar radiation to release chlorine radicals, which initiate a chain reaction with ozone and deplete the ozone layer. Accordingly, the regulations for limiting the use of such conventional CFCs have been implemented. Therefore, a research has been actively conducted to develop a CFC alternative which scarcely depletes the ozone layer.

It is an object of the present invention to provide a mixture containing a novel hydrochlorofluoropropane having 3 carbon atoms, which has various excellent properties equal to conventional CFCs and which is useful as a CFC alternative.

The present invention provides a hydrochlorofluorocarbon azeotropic or azeotropic-like mixture comprising at least one member selected from the group consisting of hydrochlorofluoropropanes of the formula I:

$CH_aCl_bF_cCF_2CH_xCl_yF_z$ (I)

wherein $a+b+c=3$, $x+y+z=3$, $a+x\geq 1$, $b+y\geq 1$, and $0\leq a,b,c,x,y,z\leq 3$, and at least one member selected from the group of compounds II consisting of halogenated hydrocarbons having a boiling point of from 20 to 85 °C other than the above hydrochlorofluoropropanes, hydrocarbons having a boiling point of from 20 to 85 °C and alcohols having from 1 to 4 carbon atoms.

The mixture of the present invention is non-flammable or hardly flammable and may take a form of an azeotropic composition or an azeotropic-like composition. Particularly when used as a solvent, it provides properties equal or superior to conventional 1,1,2-trichlorotrifluoroethane (R113). Therefore, it is very useful as an alternative for R113. Further, no substantial change in the composition was observed when boiling or evaporating. Therefore, it may be used in the same manner as a conventional single CFC, whereby it has a merit in that no substantial change in the conventional technique is required.

The hydrochlorofluoropropanes of the formula I in the present invention contain a hydrogen atom and a fluorine atom as essential elements and may further contain a chlorine atom. Specifically, they include the following compounds:

$CCl_2F_2CF_2CHCl_2$ (R224ca)
CCl_2FCF_2CHClF(R224cb)
$CF_3CF_2CHCl_2$(R225ca)
$CCl_2F_2CF_2CHClF$(R225cb)
$CCl_2F_2CF_2CH_2Cl$(R234cc)
CHF_2CF_2CHClF(R235ca)
$CH_3CF_2CCl_2F$(R243cc)
$CHF_2CF_2CH_2Cl$(R244ca)
$CH_2ClCF_2CH_2Cl$(R252ca)
$CHCl_2CF_2CH_3$(R252cb)
$CH_3CF_2CH_2Cl$(R262ca)
$CHF_2CF_2CCl_2F$(R225cc)
$CHClFCF_2CHClF$(R234ca)
$CHF_2CF_2CHCl_2$(R234cb)
$CH_2FCF_2CCl_2F$(R234cd)
$CF_3CF_2CH_2Cl$(R235cb)
$CCl_2F_2CF_2CH_2F$(R235cc)
CH_2ClCF_2CHClF(R243ca)
$CH_2FCF_2CHCl_2$(R243cb)
CH_2FCF_2CHClF(R244cb)
$CCl_2F_2CF_2CH_3$(R244cc)
$CH_2FCF_2CH_2Cl$(R253ca)
CH_3CF_2CHClF(R253cb)

CF_3CF_2CHClF(R226ca)
$CClF_2CF_2CHF_2$(R226cb)
$CCl_3CF_2CHCl_2$(R222c)
$CCl_2FCF_2CHCl_2$(R223ca)
CCl_3CF_2CHClF(R223cb)
$CCl_3CF_2CHF_2$(R224cc)
$CHCl_2CF_2CHCl_2$(R232ca)
$CCl_3CF_2CH_2Cl$(R232cb)
$CCl_2FCF_2CH_2Cl$(R233cb)
$CHCl_2CF_2CHClF$(R233ca)
$CCl_3CF_2CH_2F$(R233cc)
$CCl_3CF_2CH_3$(R242cb)
$CHCl_2CF_2CH_2Cl$(R242ca)

Among them, preferred are R225ca, R225cb, R244ca, R244cb, R235ca and R243cc.

The halogenated hydrocarbons having a boiling point of from 20 to 85°C other than the hydrochlorofluoropropanes of the formula I, include chlorinated hydrocarbons, fluorinated hydrocarbons and brominated hydrocarbons having from 1 to 4 carbon atoms.

The chlorinated hydrocarbons having from 1 to 4 carbon atoms, include dichloromethane, trichloromethane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 1-chloropropane, 2-chloro-2-methylpropane, 1,1,1-trichloroethane and 1,1-dichloroethane. The fluorinated hydrocarbons include 1,1,2-trichlorotrifluoroethane (R113), 1,1,2-trichloro-2,2-difluoroethane (R122), 1,2,2-trichloro-1,2-difluoroethane (R122a), 1,1,1-trichloro2,2-difluoroethane (R122b), 1,1-dichloro-2,2,2-trifluoroethane (R123), 1,2-dichloro-1,1-difluoroethane (R132b), 1,2-dichloro-1-fluoroethane (R141), 1,1-dichloro-1-fluoroethane (R141b) and trichlorofluoromethane (R11). Likewise, the brominated hydrocarbons include 2-bromopropane as a preferred example.

The hydrocarbons having a boiling point of from 20 to 85°C, include aliphatic, alicyclic and aromatic hydrocarbons. Preferably, they include hydrocarbons having from 5 to 8 carbon atoms such as n-pentane, isopentane, n-hexane, 2,4-dimethylpentane, cyclopentane, 2,2-dimethylbutane, 2-methylpentane, methylcyclopentane, cyclohexane and 2,3-dimethylbutane. The hydrocarbons having from 5 to 8 carbon atoms may be a mixture obtained as a petroleum fraction and may preferably be a petroleum fraction containing as the main component at least one member selected from the group consisting of cyclopentane, 2,2-dimethylbutane, 2-methylpentane and 2,3-dimethylbutane.

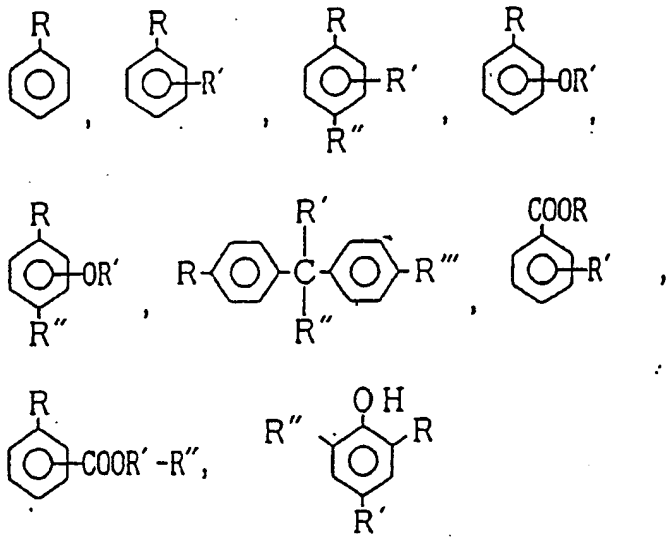
The azeotropic or azeotropic-like composition of the mixture of the present invention may vary to an extent of ±1.0% by weight depending upon the purities of the compounds to be mixed or by the influence of measuring error, etc.

To the mixture of the present invention, other components may further be incorporated, as the case requires. For example, when the mixture is used as a solvent, it may contain at least one member selected from the group consisting of hydrocarbons such as neopentane, 3-methylpentane, neohexane, hexane, 3-methylhexane, heptane, isoheptane, 2,3-dimethylpentane, 2,4-dimethylpentane, octane, 2,2,3-trimethylpentane, 2,2,4-trimethylpentane, cyclopentane, methylcyclohexane and ethylcyclohexane; chlorinated hydrocarbons such as 1,1,2-trichloroethane, 1,2-dichloroethane, trichloroethylene and tetrachloroethylene; chlorofluorinated hydrocarbons other than those of the present invention, such as 1,1-dichloro-2,3,3,3-tetrafluoropropene-1, trans-3-chloro- 1,1,1,2,4,4,5,5,5-nonafluoropentene-2, cis-3-chloro-1,1,1,2,4,4,5,5,5-nonafluoropentene-2, 1,1,1,2,2,5,5,6,6,6-decafluorohexane and tetrachloro-1,2,-difluoroethane; nitro compounds; phenols; amines; ethers; amylenes; esters; organic phosphites; epoxides; furans; alcohols; ketones; amides; and triazoles.

The content of such additional components in the mixture of the present invention is not particularly limited, but for the purpose of improving or controlling the solibility or obtaining a suitable boiling point or non-flammability, the content is usually from 0 to 50% by weight, preferably from 1 to 40% by weight. Preferably such incorporation will bring about an azeotropic or azeotropic-like composition. Further, to give the mixture a high level of stabilizing effect, it is effective to incorporate a stabilizer. The content of such additional components is usually from 1 ppm to 10% by weight, preferably from 10 ppm to 5% by weight. Further, the mixture of the present invention may further contain various cleaning assistants, surfactants, emulsifying agents, water, etc.

As the nitro compounds, those represented by the formula $R\text{-}NO_2$ wherein R is a chain or cyclic hydrocarbon group having from 1 to 6 carbon atoms and containing a saturated or unsaturated bond, may be employed. Specifically, they include nitromethane, nitroethane, 1-nitropropane, 2-nitropropane and nitrobenzene. More preferred are nitromethane and nitroethane.

As the phenols, those represented by the following formulas are preferred:

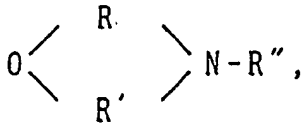


wherein each of R, R′, R″ and R‴ is OH or a chain or cyclic hydrocarbon group having from 1 to 6 carbon atoms and containing a saturated or unsaturated bond.

Specifically, they include phenol, o-cresol, m-cresol, p-cresol, thymol, p-tert-butylphenol, tert-butylcatechol, catechol, isoeugenol, o-methoxyphenol, 4,4′-dihydroxyphenyl-2,2-propane, isoamyl salicylate, benzyl salicylate, methyl salicylate and 2,6-di-t-butyl-p-cresol. More preferred are phenol, 4,4-dihydroxyphenyl-2,2-propane and 2,6-di-t-butyl-p-cresol.

As the amines, those represented by the following formulas are preferred:

$R\text{-}N(R')_2$, $(R)_2\text{-}N(R')_2$, $(R)_2\text{-}NR'$, $(R)_3N$, RN,



$(R)_2N\text{-}R'\text{-}N\text{-}(R'')_2$

$R\text{-}CHN(R')_2\text{-}R'\text{-}N\text{-}(R'')_2$

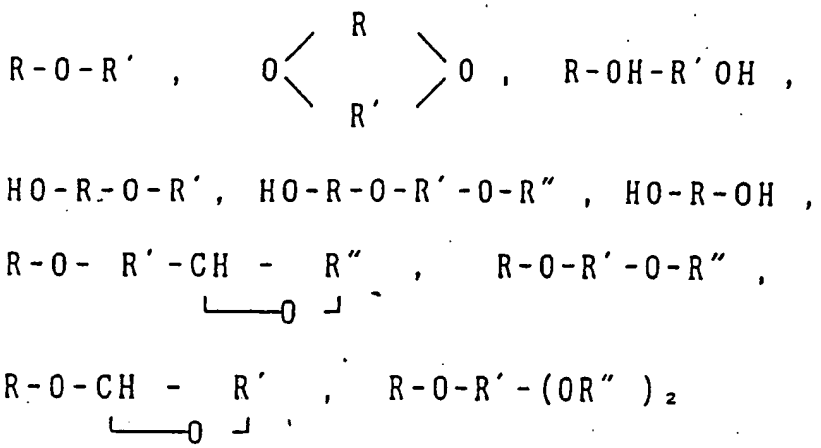
$(R)_2N\text{-}R'\text{-}NH\text{-}R''\text{-}N\text{-}(R')_2$

$(R)_2N\text{-}(R'NH)_4\text{-}R''$, R-NH-R′, and $(R)_2\text{-}N\text{-}OR'$

wherein each of R, R′, R″ and R‴ is a hydrogen atom or a chain or cyclic hydrocarbon group having from 1 to 8 carbon atoms and containing a saturated or unsaturated bond.

Specifically, they include pentylamine, hexylamine, diisopropylamine, diisobutylamine, di-n-propylamine, diallylamine, triethylamine, n-methylaniline, pyridine, picoline, morpholine, N-methylmorpholine, triallylamine, allylamine, α-methylbenzylamine, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, propylamine, isopropylamine, sec-butylamine, tert-butylamine, dibutylamine, tributylamine, dipentylamine, tripentylamine, 2-ethylhexylamine, aniline, N,N-dimethylaniline, N,N-diethylaniline, ethylenediamine, propylenediamine, diethylenetriamine, tetraethylenepentamine, benzylamine, dibenzylamine, diphenylamine and diethylhydroxylamine. More preferred are diisopropylamine and diallylamine.

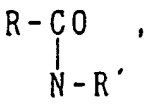
As the ethers, those represented by the following formulas are preferred:



wherein each of R, R′ and R″ is a chain or cyclic hydrocarbon group having from 1 to 10 carbon atoms and containing a saturated or unsaturated bond. Specifically, they include 1,4-dioxane, 1,2-butanediol, isopropyl ether, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, dipropylene glycol methyl ether, ethyl isobutyl ether, ethyl isopentyl ether, ethyl naphthyl ether, ethyl vinyl ether, ethyl phenyl ether, anisole, anethole, ethyl propargyl ether, ethyl propyl ether, ethyl methyl ether, ethylene glycol, methyl glycidyl ether, ethylene glycol diethyl ether, ethylene glycol diphenyl ether, ethylene glycol dimethyl ether, ethylene glycol monophenyl ether, ethylene glycol monobutyl ether, ethylene glycol monobenzyl ether, dipentyl ether, allyl ethyl ether, diisopentyl ether, diallyl ether, butyl glycidyl ether, allyl glycidyl ether, dipropyl ether, ethyl glycidyl ether, vinyl glycidyl ether, dimethyl ether, diethyl ether, di-n-propyl ether, dibutyl ether, 1,2-dimethoxyethane, trimethoxyethane, and triethoxyethane. More preferred are 1,4-dioxane, butyl glycidyl ether and 1,2-dimethoxyethane.

As the amylenes, α-amylene, β-amylene, γ-amylene, α-isoamylene and β-isoamylene are preferred. More preferred is β-amylene.

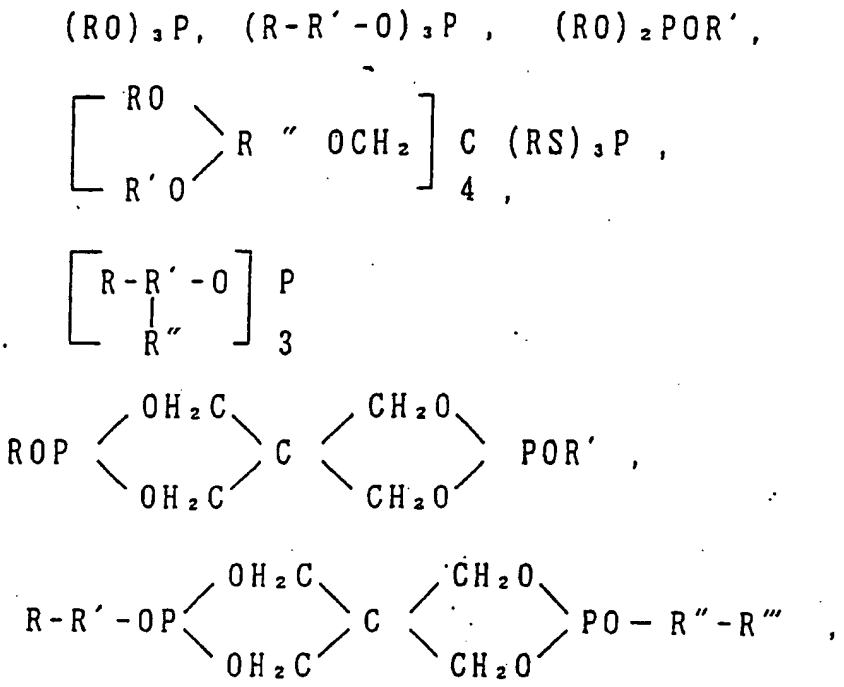
As the esters, those represented by the following formulas are preferred:
R-COO-R′,



(R′)$_2$-N-COO-R′, and RO-R′-COOR″
wherein each of R, R′ and R″ is a hydrogen atom or a chain or cyclic hydrocarbon group having from 1 to 6 carbon atoms and containing a saturated or unsaturated bond.

Specifically, they include methyl acetate, ethyl acetate, propyl acetate, n-butyl acetate, isobutyl acetate, isopropyl acetate, ethyl acrylate, 2-hydroxyethyl methacrylate, methyl acrylate, butyl acrylate, phenyl acrylate, allyl acrylate, caprolactam, ethyl carbamate, methyl carbamate, and methyl salicylate. More preferred are methyl acetate and methyl salicylate.

As the organic phosphites, those represented by the following formula are preferred:



wherein each of R, R′, R″ and R‴ is a hydrogen atom or a saturated or unsaturated chain or cyclic hydrocarbon group having from 1 to 18 carbon atoms. Specifically, they include triphenolphosphite, tris-(nonylphenyl)phosphite, triethylphosphite, tris(2-ethylhexyl)phosphite, tridecylphosphite, tributylphosphite, diphenylmono(2-ethylhexyl)phosphite, diphenylmonodecylphosphite, diphenylmonotridecylphosphite, dilaurylhydrogen phosphite, diphenylhydrogen phosphite, tetraphenyldipropylene glycol pentaerythritol tetraphosphite, trilauryltrithiophosphite, bis(tridecyl)pentaerythritol diphosphite, bis(nonylphenyl)-pentaerythritol diphosphite, tristearyl phosphite, distearyl pentaerythritol diphosphite, and tris(2,4-di-tert-butylphenyl)phosphite. More preferred are triphenylphosphite and tributylphosphite.

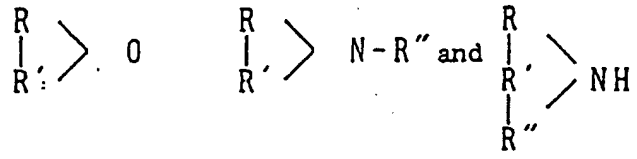
As the epoxides, those represented by the following formulas are preferred:

RO and XRO

wherein R is a saturated or unsaturated chain or cyclic hydrocarbon group having from 1 to 8 carbon atoms, and X is a halogen atom.

Specifically, they include 1,2-butylene oxide, epichlorohydrin, propylene oxide, 2,3-butylene oxide and styrene oxide. More preferred are 1,2-butylene oxide and epichlorohydrin.

As the furans, those represented by the following formulas are preferred:



wherein each of R, R′ and R″ is a saturated or unsaturated hydrocarbon group having from 1 to 2 carbon atoms. Specifically they include tetrahydrofuran, n-methylpyrrole, 2-methylpyrrole and 3-methylpyrrole. More preferred is N-methylpyrrole.

As the alcohols which are mainly used as stabilizers, those presented by the following formulas are preferred:

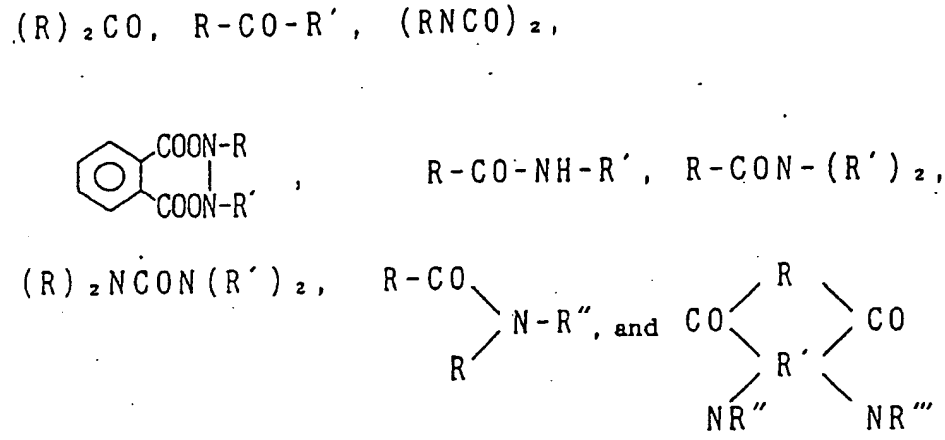
R-OH, NH_2-R-OH, R-O-R′-OH and R-R′-OH

wherein each of R and R′ is a saturated or unsaturated chain or cyclic hydrocarbon group having from 1 to

6 carbon atoms.

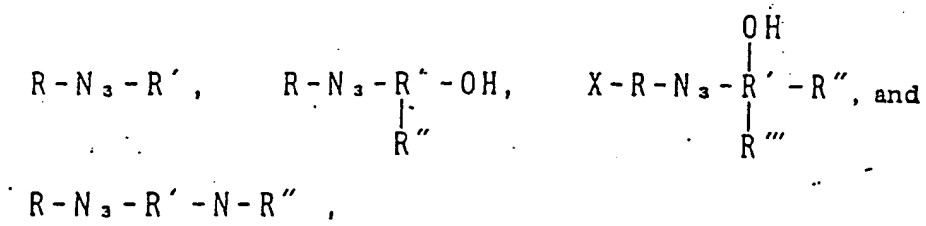
Specifically, they include, methanol, ethanol, secbutanol, tert-butanol, allylalcohol, benzylalcohol, propanol, isopropanol, tert-amylalcohol, 1-amino-2-propanol, propargylalcohol, isobutanol, butanol, 3-methylpentyn-3-ol, 1-methoxy-2-propanol, 3-methyl-1-butyn-3-ol, 2-methyl-3-butyn-3-ol, pentyl alcohol, hexanol, heptanol and octanol. More preferred are secbutanol and propargyl alcohol.

As the ketones and amides, those represented by the following formulas are preferred:



wherein each of R, R′, R″ and R‴ is a hydrogen atom or a saturated or unsaturated hydrocarbon group having from 1 to 4 carbon atoms. Specificaly, they include acetone, methyl ethyl ketone, methyl isobutyl ketone, azodicarbonamide, maleic acid hydrazine, phthalic acid hydrazine, formamide, N-methylformamide, N,N-dimethylformamide, N-methylpropropioneamide, 2-pyrrolidone, N,N,N′-tetramethylurea and N-methylpyrrolidone. More preferred are methyl isobutyl ketone and 2-pyrrolidone.

As the triazoles, those presented by the following formulas are preferred:



wherein each of R, R′, R″ and R‴ is a hydrogen atom or a saturated or unsaturated chain or cyclic hydrocarbon group having from 1 to 16 carbon atoms, and X is a halogen atom.

Specifically, they include 2-(2′-hydroxy-5′-methylphenyl)benzotriazole, 2-(2′-hydroxy-3′-tert-butyl-5′-methylphenyl)-5-chlorobenzotriazole, 1,2,3-benzotriazole, and 1-[(N,N-bis-2-ethylhexyl)aminomethyl]-benzotriazole. More preferred is 1,2,3-benzotriazole.

The hydrochlorofluorocarbon azeotropic or azeotropic-like mixture of the present invention is useful for various purposes, for example, as a blowing agent and so on, like conventional CFCs. It is particularly useful as a solvent, since it provides a solvency equivalent or superior to conventional R113. Specific applications as the solvent include a removing agent for flux, grease, oil, wax or ink, a coating solvent, an extracting agent, a cleaning or water-removing agent for various articles made of glass, ceramics, plastic, rubber or metal, particularly for semiconductor devices, electronic components, electronic circuit boards, electrical cevices, precision machine parts or optical lenses. Further, it is useful as a resist developer, a resist-removing agent or a buff polishing and cleaning agent. As a cleaning method, manual wiping, dipping, spraying, shaking, ultrasonic cleaning or vapor cleaning may be employed.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by such specific Examples.

EXAMPLES 1 to 152

1,000 g of a mixture as identified in Table 1 was charged in a distillation flask, and using a packed distillation column which contained approximately 20 theoretical plates, distillation was conducted under atmospheric pressure. The fractions thereby obtained were measured by gas chromatography, whereby the presence of an azeotropic composition was found.

On the other hand, the azeotropic-like composition was obtained from the composition after repeating the evaporation and condensation of a mixture as identified in Table 1 for 3 days by an open system cleaning sump.

A SUS-304 test piece (25 mm x 30 mm x 2 mm in thickness) was immersed in machine oil (CQ-30, manufactured by Nippon Sekiyu K.K.) and then immersed in the azeotropic mixture of the present invention for 5 minutes. The results are shown in Table 1, wherein symbol A-◎ indicates that the machine oil can be removed satisfactorily at the same level as R113.

A single sided printed circuit board (50 mm x 100 mm x 1.6 mm in thickness) was coated with a flux (Tamura F-AL-4, manufactured by Tamura Seisakusho) and heated at 200°C for 2 minutes in a convection oven. Then, it was immersed in the azeotropic mixture of the present invention for one minute. The results are shown in Table 1, in which symbol B-◎ indicates that the flux can be removed satisfactorily at the same level as R113/ethanol = 96.2 wt%/3.8 wt%.

A glass plate (30 mm x 18 mm x 5 mm in thickness) was immersed in deionized water and then immersed in the azeotropic mixture of the present invention for 20 seconds for removal of water. The glass plate withdrawn, was immersed in dry methanol, whereby the removal of water was determined from the increase of the water content in methanol. The results are shown in Table 1, in which symbol C-◎ indicates that the water can be removed satisfactorily at the same level as R113/methanol = 93.6 wt%/6.4 wt%.

Table 1

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
1	R225ca R141b	51.1 32	30 70	31	25 75	5-45 55-95	A-◎
2	R225ca R113	51.1 47.6	40 60	44	42 58	22-62 38-78	A-◎
3	R225ca R122	51.1 71.9	80 20	52	78 22	58-98 2-42	A-◎
4	R225ca R132b	51.1 46.8	52 48	42	50 50	30-70 30-70	A-◎
5	R225ca Dichloro-methane	51.1 39.8	50 50	34	47 53	27-67 33-73	B-◎
6	R225cb R141b	56.1 32	20 80	32	16 84	1-36 64-99	A-◎
7	R225cb Dichloro-methane	56.1 39.8	50 50	36	43 57	33-53 47-67	B-◎
8	R225cb R132b	56.1 46.8	42 58	43	39 61	19-59 41-81	A-◎
9	R225cb R122	56.1 71.9	80 20	55	78 22	58-98 2-42	A-◎
10	R225cb R113	56.1 47.6	30 70	46	32 68	12-52 48-88	A-◎
11	R244ca R141b	54 32	15 85	32	13 87	1-33 67-99	A-◎
12	R244ca Dichloro-methane	54 39.8	50 50	35	38 62	18-58 42-82	A-◎ B-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
13	R244ca R122	54 71.9	80 20	55	83 17	63-99 1-37	A-◎
14	R244ca R132b	54 46.8	42 58	44	38 62	18-58 42-82	A-◎
15	R244ca R113	54 47.6	20 80	47	26 74	6-46 54-94	A-◎
16	R225ca Cyclo-pentane	51.1 49.3	70 30	45	66 34	46-98 2-54	A-◎
17	R225cb Cyclo-pentane	56.1 49.3	58 42	47	55 45	35-98 2-65	A-◎
18	R244ca 2,2-dimethyl-butane	54 49.7	50 50	50	48 52	28-98 2-72	A-◎
19	R225cb 2,2-dimethyl-butane	56.1 49.7	25 75	50	21 79	11-98 2-89	A-◎
20	R244ca Cyclo-pentane	54 49.3	55 45	47	50 50	30-98 2-70	A-◎
21	R225ca 2,2-dimethyl-butane	51.1 49.7	60 40	49	56 44	36-98 2-64	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
22	R225ca 2-bromopropane	51.1 59.4	60 40	47	66 34	46-86 14-54	A-◎
23	R225cb 2-bromopropane	56.1 59.4	60 40	49	58 42	38-78 22-62	A-◎
24	R244ca 2-bromopropane	54 59.4	50 50	48	55 45	35-75 25-65	A-◎
25	R244cb 2-bromopropane	58 59.4	60 40	50	50 50	30-70 30-70	A-◎
26	R235ca 2-bromopropane	43.9 59.4	70 30	42	74 26	54-94 6-46	A-◎
27	R243cc 2-bromopropane	60.2 59.4	40 60	52	50 50	30-70 30-70	A-◎
28	R225cb 2-methylpentane	56.1 60.3	90 10	-	- -	50-99 1-50	A-◎
29	R244ca 2-methylpentane	54 60.3	90 10	55	91 9	71-99 1-29	A-◎
30	R244cb 2-methylpentane	58 60.3	70 30	55	72 28	52-98 2-48	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
31	R243cc 2-methylpentane	60.2 60.3	70 30	61	74 26	54-99 1-46	A-◎
32	R225cb 2,3-dimethylbutane	56.1 58.0	80 20	56	78 22	58-98 2-42	A-◎
33	R244ca 2,3-dimethylbutane	54 58.0	80 20	53	76 24	56-96 4-44	A-◎
34	R244cb 2,3-dimethylbutane	58 58.0	60 40	55	63 37	43-95 5-57	A-◎
35	R225ca 2,3-dimethylbutane	51.1 58.0	90 10	-	- -	85-99 1-15	A-◎
36	R243cc 2,3-dimethylbutane	60.2 58.0	90 10	-	- -	50-95 5-50	A-◎
37	R225ca trans-1,2-dichloroethylene	51.1 47.7	60 40	44	57 43	37-77 23-63	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
38	R225cb trans-1,2-dichloroethylene	56.1 47.7	50 50	46	47 53	27-67 33-73	A-◎
39	R244ca trans-1,2-dichloroethylene	54 47.7	50 50	45	46 54	27-66 34-74	A-◎
40	R244cb trans-1,2-dichloroethylene	58 47.7	45 55	46	40 60	20-60 40-80	A-◎
41	R235ca trans-1,2-dichloroethylene	43.9 47.7	70 30	41	66 34	46-86 14-54	A-◎
42	R243cc trans-1,2-dichloroethylene	60.2 47.7	40 60	45	42 58	22-62 38-78	A-◎
43	R225ca cis-1,2-dichloroethylene	51.1 60.6	80 20	50	78 22	58-98 2-42	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
44	R225cb cis-1,2-dichloroethylene	56.1 60.6	70 30	53	69 31	59-79 21-41	A-◎
45	R244ca cis-1,2-dichloroethylene	54 60.6	70 30	51	67 33	47-87 13-53	A-◎
46	R244cb cis-1,2-dichloroethylene	58 60.6	60 40	54	59 41	39-79 21-61	A-◎
47	R235ca cis-1,2-dichloroethylene	43.9 60.6	90 10	45	94 6	74-99 1-26	A-◎
48	R243cc cis-1,2-dichloroethylene	60.2 60.6	60 40	52	58 42	38-78 22-62	A-◎
49	R244cb R113	58 47.6	10 90	48	12 88	2-32 68-98	A-◎
50	R235ca R113	43.9 47.6	60 40	42	56 44	36-76 24-64	A-◎
51	R244cb Dichloromethane	58 39.8	30 70	36	33 67	13-53 47-87	A-◎
52	R235ca Dichloromethane	43.9 39.8	50 50	32	53 47	33-73 27-67	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
53	R243cc Dichloromethane	60.2 39.8	50 50	38	30 70	10-50 50-90	A-◎
54	R244cb Cyclopentane	58 49.3	40 60	48	43 57	23-99 1-77	A-◎
55	R235ca Cyclopentane	43.9 49.3	80 20	42	77 23	67-99 1-33	A-◎
56	R243cc Cyclopentane	60.2 49.3	25 75	49	30 70	10-99 1-90	A-◎
57	R244cb 2,2-dimethylbutane	58 49.7	40 60	50	34 66	14-99 1-86	A-◎
58	R235ca 2,2-dimethylbutane	43.9 49.7	80 20	43	81 19	61-99 1-39	A-◎
59	R244cb R122	58 71.9	80 20	58	75 25	55-95 5-45	A-◎
60	R244cb R132b	58 46.8	30 70	45	29 71	9-49 51-91	A-◎
61	R235ca R123	43.9 27.1	20 80	28	14 86	1-34 66-99	A-◎
62	R235ca R132b	43.9 46.8	20 80	39	57 43	37-77 23-63	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
63	R235ca R141b	43.9 32	30 70	30	34 66	14-54 46-86	A-◎
64	R243cc R122	60.2 71.9	80 20	60	77 23	57-97 3-43	A-◎
65	R243cc R132b	60.2 46.8	20 80	46	24 76	4-44 56-96	A-◎
66	R225ca R141	51.1 75.7	90 10	52	95 5	75-99 1-25	A-◎
67	R225cb R141	56.1 75.7	90 10	56	89 11	69-99 1-31	A-◎
68	R244cb R141	58 75.7	85 15	59	90 10	70-99 1-30	A-◎
69	R225ca Methanol	51.1 64.5	97 3	46	94.6 5.4	75-99 1-25	A-◎ B-◎ C-◎
70	R225cb Ethanol	56.1 78.3	97 3	53.8	95.6 4.4	74-99.5 0.5-26	A-◎ B-◎ C-◎
71	R225cb Iso-propanol	56.1 82.4	97 3	54.9	97.9 2.1	77-99 1-23	A-◎ B-◎ C-◎
72	R225cb Methanol	56.1 64.5	95 5	47.2	93.3 6.7	74-99 1-26	A-◎ B-◎ C-◎
73	R225ca R225cb Ethanol	51.1 56.1 78.3	90 5 5	50	94.8 2.7 2.5	14-98 1-85 1-16	A-◎ B-◎ C-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
74	R225ca R225cb Methanol	51.1 56.1 64.7	89 6 5	46	89.8 5.6 4.6	14-98 1-85 1-16	A-◎ B-◎ C-◎
75	R225ca Ethanol	51.1 78.3	98.5 1.5	50	97.3 2.7	75-99.5 0.5-25	A-◎ B-◎ C-◎
76	R225ca Iso-propanol	51.1 82.4	-	-	-	76-99 1-24	A-◎ B-◎ C-◎
77	R225ca R113 Dichloro-methane	51.1 47.6 39.8	35 15 50	-	38 15 47	15-61 8-44 34-70	A-◎ B-◎
78	R225cb R113 R132b	56.1 47.6 46.8	25 35 40	-	26 35 39	6-37 22-52 27-51	A-◎
79	R225ca R113 R132b	51.1 47.6 46.8	35 25 40	-	32 29 39	22-55 10-46 21-55	A-◎
80	R225cb R113 Dichloro-methane	56.1 47.6 39.8	25 25 50	-	26 24 50	8-38 8-47 34-63	A-◎ B-◎
81	R244ca R113 Dichloro-methane	54 47.6 39.8	25 20 55	-	25 19 56	6-33 9-41 43-68	A-◎ B-◎
82	R244ca R113 R132b	54 47.6 46.8	20 30 50	-	19 32 49	4-39 6-53 30-67	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
83	R225ca R113 trans-1,2-dichloroethylene	51.1 47.6 47.7	40 20 40	-	41 22 37	28-52 7-39 25-48	A-◎ B-◎
84	R244ca R113 2-bromopropane	54 47.6 59.4	30 60 10	-	25 62 13	8-36 48-85 3-28	A-◎ B-◎
85	R225ca R113 2-bromopropane	51.1 47.6 59.4	40 50 10	-	42 47 11	29-60 11-61 3-29	A-◎ B-◎
86	R244ca R113 cis-1,2-dichloroethylene	54 47.6 60.6	20 60 20	-	22 58 20	4-38 40-77 9-32	A-◎ B-◎
87	R225ca R113 cis-1,2-dichloroethylene	56.1 47.6 60.6	35 50 15	-	32 53 15	19-43 39-60 8-22	A-◎ B-◎
88	R225ca R113 cis-1,2-dichloroethylene	51.1 47.6 60.6	40 45 15	-	42 45 13	25-54 38-58 8-22	A-◎ B-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
89	R244ca R113 trans-1,2-dichloroethylene	54 47.6 47.7	35 22 48	-	34 20 46	5-45 4-60 26-59	A-◎ B-◎
90	R225cb R113 trans-1,2-dichloroethylene	56.1 47.6 47.7	35 25 40	-	36 27 37	27-51 6-44 29-48	A-◎ B-◎
91	R225cb R113 2-bromopropane	56.1 47.6 59.4	35 55 10	-	34 56 10	22-43 38-68 3-26	A-◎ B-◎
92	R225cb R113 Cyclopentane	56.1 47.6 49.3	35 55 10	-	34 55 11	20-53 8-72 1-40	A-◎
93	R225ca R113 Cyclopentane	51.1 47.6 49.3	40 50 10	-	41 52 7	28-65 13-68 2-35	A-◎
94	R244ca R113 2,2-dimethylbutane	54 47.6 49.7	25 70 5	-	23 71 6	17-46 8-77 2-56	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
95	R225ca R113 1-chloropropane	51.1 47.6 46.6	50 20 30	-	52 16 32	42-61 7-55 2-43	A-◎ B-◎
96	R225cb R113 1-chloropropane	56.1 47.6 46.6	40 30 30	-	42 27 31	23-44 8-70 2-47	A-◎ B-◎
97	R244ca R113 2-chloro-2-methylpropane	54 47.6 50.7	20 60 20	-	22 57 21	4-33 41-78 8-31	A-◎ B-◎
98	R244ca R113 Cyclopentane	54 47.6 49.3	30 50 20	-	27 50 23	5-45 9-74 12-46	A-◎
99	R225ca R113 2-chloro-2-methylpropane	51.1 47.6 50.7	45 50 5	-	40 55 5	28-56 12-64 2-32	A-◎ B-◎
100	R225cb R113 2-chloro-2-methylpropane	56.1 47.6 50.7	30 60 10	-	31 58 11	17-38 41-75 2-21	A-◎ B-◎
101	R224ca R113 1-chloropropane	54 47.6 46.6	35 20 45	-	36 19 45	9-39 9-84 2-60	A-◎ B-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
102	R225ca R225cb 2-methylpentane	51.1 56.1 60.3	90 5 5	-	90 7 3	36-97 1-51 1-16	A-◎
103	R225ca R225cb 2,3-dimethylbutane	51.1 56.1 58.0	85 10 5	-	88 8 4	6-94 1-83 1-26	A-◎
104	R225ca R225cb 2-chloro-2-methylpropane	51.1 56.1 50.7	50 10 40	-	50 12 38	6-67 4-67 1-58	A-◎ B-◎
105	R225ca R225cb 1-chloropropane	51.1 56.1 46.6	40 15 45	-	41 14 45	7-56 7-61 1-54	A-◎ B-◎
106	R225ca R225cb 2-bromopropane	51.1 56.1 59.4	55 10 35	-	54 10 36	6-66 5-64 10-48	A-◎ B-◎
107	R225ca R225cb cis-1,2-dichloroethylene	51.1 56.1 60.6	60 10 30	-	58 12 30	6-70 4-74 10-38	A-◎ B-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
108	R225ca R225cb trans-1,2-dichloroethylene	51.1 56.1 47.7	40 15 45	-	42 13 45	8-57 6-54 10-59	A-◎ B-◎
109	R225ca R225cb R122	51.1 56.1 71.9	80 10 10	-	80 8 12	40-89 2-37 3-23	A-◎ B-◎
110	R225ca R225cb R141	51.1 56.1 75.7	80 10 10	-	84 8 8	44-92 2-41 1-17	A-◎ B-◎
111	R225ca R225cb R132b	51.1 56.1 46.8	35 10 55	-	36 11 53	6-44 4-44 44-73	A-◎ B-◎
112	R225ca R141b Dichloromethane	56.1 32 39.8	25 65 10	-	20 67 13	8-31 36-88 3-38	A-◎ B-◎
113	R225ca R141b Dichloromethane	51.1 32 39.8	30 60 10	-	26 62 12	8-41 32-84 3-31	A-◎ B-◎
114	R225ca R141b R123	51.1 32 27.1	15 5 80	-	12 7 81	6-33 2-33 44-86	A-◎ B-◎
115	R225ca R225cb R113	51.1 56.1 47.6	30 10 60	-	33 9 58	5-47 3-42 5-79	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
116	R225ca R225cb Dichloromethane	51.1 56.1 39.8	25 21 55	-	25 21 54	9-49 8-39 5-70	A-◎ B-◎
117	R244ca R141b Dichloromethane	54 32 39.8	15 70 15	-	16 68 16	6-31 38-90 3-40	A-◎ B-◎
118	R244ca R225cb 2-bromopropane	54 56.1 59.4	20 40 40	-	21 42 37	5-58 7-66 5-54	A-◎ B-◎
119	R244ca R225cb cis-1,2-dichloroethylene	54 56.1 60.6	30 40 30	-	31 35 34	4-58 7-71 4-43	A-◎ B-◎
120	R244ca R225cb 1-chloropropane	54 56.1 46.6	15 40 45	-	15 39 46	8-58 9-65 5-71	A-◎ B-◎
121	R244ca R225cb 2-chloro-2-methylpropane	54 56.1 50.7	20 30 50	-	22 32 46	7-55 8-56 5-74	A-◎ B-◎
122	R244ca R225cb 2,3-dimethylbutane	54 56.1 58	60 20 20	-	62 20 18	29-87 6-68 2-29	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
123	R244ca R225cb R132b	54 56.1 46.8	20 20 60	-	18 24 58	5-42 7-50 41-80	A-◎ B-◎
124	R244ca R225cb trans-1,2-dichloroethylene	54 56.1 47.7	30 25 45	-	30 26 44	5-55 8-57 5-61	A-◎ B-◎
125	R244ca R225cb Cyclopentane	54 56.1 49.3	25 30 45	-	25 32 45	8-56 9-55 5-69	A-◎
126	R244ca R225cb Dichloromethane	54 56.1 39.8	20 20 60	-	17 24 59	7-35 9-42 45-73	A-◎ B-◎
127	R244ca R225ca 2,2-dimethylbutane	54 51.1 49.7	40 20 40	-	39 19 42	7-61 8-71 5-72	A-◎
128	R244ca R225ca Dichloromethane	54 51.1 39.8	10 30 60	-	12 34 54	5-41 9-48 40-73	A-◎ B-◎
129	R244ca R225ca R132b	54 51.1 46.8	10 40 50	-	9 40 51	2-37 7-50 35-72	A-◎ B-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
130	R244ca R225ca R141	54 51.1 75.7	25 70 5	-	24 70 6	3-49 47-95 0.1-17	A-◎ B-◎
131	R244ca R225ca Cyclo-pentane	54 51.1 49.3	10 55 35	-	11 55 34	5-55 9-67 3-53	A-◎
132	R244ca R225ca R122	54 51.1 71.9	20 70 10	-	21 70 9	3-59 36-93 1-22	A-◎ B-◎
133	R244ca R225ca trans-1,2-dichloro-ethylene	54 51.1 47.7	10 50 40	-	11 47 42	3-69 8-78 3-54	A-◎ B-◎
134	R244ca R225ca cis-1,2-dichloro-ethylene	54 51.1 60.6	8 62 30	-	10 60 30	3-59 7-75 3-38	A-◎ B-◎
135	R244ca R225ca 2-bromo-propane	54 51.1 59.4	10 60 30	-	8 58 34	3-58 6-71 3-44	A-◎ B-◎
136	R244ca R225cb R141	54 56.1 75.7	45 45 10	-	47 47 6	22-86 6-72 1-21	A-◎ B-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
137	R225ca R225cb Cyclopentane	51.1 56.1 49.3	50 10 40	-	48 15 37	10-88 8-70 3-58	A-◎
138	R244ca R225cb R122	54 56.1 71.9	50 40 10	-	45 45 10	8-83 6-84 3-28	A-◎ B-◎
139	R244ca R225ca 2,3-dimethylbutane	54 51.1 58	30 65 5	-	29 67 4	3-84 13-94 0.1-19	A-◎
140	R244ca R225ca 1-chloropropane	54 51.1 46.6	10 50 40	-	11 48 41	3-48 7-62 3-56	A-◎ B-◎
141	R244ca R225ca 2-chloro-2-methylpropane	54 51.1 50.7	10 60 30	-	10 54 36	3-56 6-72 3-54	A-◎ B-◎
142	R244ca R225cb 2,2-dimethylbutane	54 56.1 49.7	45 10 45	-	42 14 44	7-76 8-62 3-73	A-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
143	R244ca Methanol	54 64.7	-	-	-	76-99 1-24	A-◎ B-◎
144	R244ca Ethanol	54 78.3	-	-	-	77-99 1-23	A-◎ B-◎
145	R244ca Iso-propanol	54 82.4	-	-	-	79-99 1-21	A-◎ B-◎
146	R225ca R244ca Ethanol	51.1 54 78.3	-	-	-	50-80 10-40 1-10	A-◎ B-◎
147	R225cb R224ca Ethanol	56.1 54 78.3	-	-	-	40-80 10-50 1-10	A-◎ B-◎
148	R225ca R225cb R244ca Ethanol	51.1 56.1 54 78.3	-	-	-	5-99 3-99 1-69 1-35	A-◎ B-◎
149	R225ca R244ca Methanol	51.1 54 64.7	-	-	-	50-80 10-40 1-10	A-◎ B-◎
150	R225cb R244ca Methanol	56.1 54 64.7	-	-	-	40-80 10-50 1-10	A-◎ B-◎
151	R225ca R225cb R244ca Methanol	51.1 56.1 54 64.7	-	-	-	5-99 3-99 1-69 1-35	A-◎ B-◎

Table 1 (continued)

Examples	Mixtures	B.P. (°C)	Charged composition (wt%)	Boiling point of Azeotrope (°C)	Azeotropic composition (wt%)	Azeotropic-like composition (wt%)	Test results
152	R225ca R225cb Isopropanol	51.1 56.1 82.4	-	-	-	1-98 1-98 1-16	A-◎ B-◎

REFERENCE EXAMPLES

For the purpose of ascertaining the effects of the azeotropic-like mixture of the present invention for stabilization, the following test was applied to the mixture as identified in Table 2.

In accordance with JIS K1600, a metal test piece was placed in both the liquid phase portion and the gas phase portion of the stabilized mixture as identified in Table 2, and after 48 hours, the state of corrosion of the test piece was inspected. The results are shown in Table 2.

Azeotropic-like mixture

AA: R225ca/R225cb/methanol = 47 wt%/47 wt%/6 wt%

Stabilizer

NM: Nitromethane
DIPA: Diisopropylamine
Am: β-Amylene
TPH: Triphenylphosphite
DME: 1,2-Dimethoxyethane
s-Bu: sec-Butanol
ECH: Epichlorohydrin
BHT: 2,6-Di-t-butyl-o-cresol
BTA: 1,2,3-Benzotriazole
PH: Phenol
DO: 1,4-Dioxane
MeA: Methyl acetate
BO: 1,2-Buthyleneoxide
MP: N-methylpyrrole
MIBK: Methyl isobutyl ketone
i-Bu: Isobutanol

Appearance of test piece

◎: No corrosion
O: No substantial corrosion
Δ : Corrosion slightly observed
X: Substantial corrosion observed.

Table 2

Reference Examples	Stabilized mixture (wt%)	Corrosion of test piece		
		Fe	Cu	Ag
AA01	AA(99.5)/PH(0.5)	◎	○	○
AA02	AA(99.5)/DIPA(0.5)	◎	○	○
AA03	AA(99.5)/Am(0.5)	◎	○	○
AA04	AA(99.5)/TPH(0.5)	◎	○	○
AA05	AA(99.5)/MP(0.5)	◎	○	○
AA06	AA(99.5)/BTA(0.5)	○	◎	○
AA07	AA(99)/NM(1)	◎	○	○
AA08	AA(99)/DO(1)	◎	○	○
AA09	AA(99)/MeA(1)	◎	○	○
AA10	AA(99)/BO(1)	◎	○	○
AA11	AA(99)/DME(1)	◎	○	○
AA12	AA(99)/s-Bu(1)	◎	○	○
AA13	AA(99)/MIBK(1)	◎	○	○
AA14	AA(99)/ECH(1)	◎	○	○
AA15	AA(98.5)/NM(1)/BTA(0.5)	◎	◎	◎
AA16	AA(97.5)/NM(1)/BO(1)/BHT(0.5)	◎	◎	○
AA17	AA(97)/NM(1)/BO(1)/BHT(0.5/BTA(0.5)	◎	◎	◎
AA18	AA(96)/NM(1)/BTA(0.5)/BO(1)/i-Bu(1)/BHT(0.5)	◎	◎	◎
Comparative Example	AA(100)	◎	△	△

The hydrochlorofluorocarbon azeotropic or azeotropic-like mixture of the present invention is non-flammable or hardly flammable and has excellent properties equal or superior to conventional CFCs. Further, the mixture shows no substantial change in the composition during boiling and evaporating, since it has an azeotropic composition or an azeotropic-like composition, and it can be used in the same manner as a conventional single CFC and thus has a merit that it requires no substantial change of the conventional technique. Further, it is excellent in the properties for dissolving and removing a flux or oil like R113 which is commonly used as a solvent, and thus it is useful as a cleaning agent which may be an alternative for R113.

Claims

1. A hydrochlorofluorocarbon azeotropic or azeotropic-like mixture comprising at least one member selected from the group consisting of hydrochlorofluoropropanes of the formula I:
$CH_aCl_bF_cCF_2CH_xCl_yF_z$ (I)
wherein $a+b+c=3$, $x+y+z=3$, $a+x\geq 1$, $b+y\geq 1$, and $0\leq a,b,c,x,y,z\leq 3$, and at least one member selected from the group of compounds II consisting of halogenated hydrocarbons having a boiling point of from 20 to 85° C other than said hydrochlorofluoropropanes, hydrocarbons having a boiling point of from 20 to 85° C and alcohols having from 1 to 4 carbon atoms.

2. The mixture according to Claim 1, wherein the hydrochlorofluoropropanes of the formula I are 3,3-dichloro-1,1,1,2,2-pentafluoropropane (R225ca), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (R225cb), 3-chloro

1,1,2,2-tetrafluoropropane (R244ca), 1-chloro-1,2,2,3-tetrafluoropropane (R244cb), 3-chloro-1,1,2,2,3-pentafluoropropane (R235ca) and 1,1-dichloro-1,2,2-trifluoropropane (R243cc).

3. The mixture according to Claim 1, wherein the halogenated hydrocarbons having a boiling point of from 20 to 85°C other than said hydrochlorofluoropropanes are chlorinated hydrocarbons, fluorinated hydrocarbons and brominated hydrocarbons having from 1 to 4 carbon atoms.

4. The mixture according to Claim 1, wherein the hydrocarbons having a boiling point of from 20 to 85°C have from 5 to 8 carbon atoms.

5. The mixture according to Claim 1, wherein the alcohols having from 1 to 4 carbon atoms are methanol, ethanol and isopropanol.

6. The mixture according to Claim 3, wherein the chlorinated hydrocarbons having from 1 to 4 carbon atoms are dichloromethane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 1-chloropropane and 2-chloro-2-methylpropane.

7. The mixture according to Claim 3, wherein the fluorinated hydrocarbons are 1,1,2-trichlorotrifluoroethane (R113), 1,1,2-trichloro-2,2-difluoroethane (R122), 1,1-dichloro-2,2,2-trifluoroethane (R123), 1,2-dichloro-1,1-difluoroethane (R132b), 1,2-dichloro-1 fluoroethane (R141) and 1,1-dichloro-1-fluoroethane (141b).

8. The mixture according to Claim 3, wherein the brominated hydrocarbon is 2-bromopropane.

9. The mixture according to Claim 4, wherein the hydrocarbons having from 5 to 8 carbon atoms are cyclopentane, 2,2-dimethylbutane, 2-methylpentane and 2,3-dimethylbutane.

10. The mixture according to Claim 1, which comprises R225ca and at least one member selected from the group consisting of R141, R141b, R141b/dichloromethane, R141b/R123, dichloromethane, R122, R132b, R113, R113/R132b, R113/dichloromethane, R113/2-bromopropane, cyclopentane, 2,2-dimethylbutane, 2-methylpentane, 2-bromopropane, 2,3-dimethylbutane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, R113/cyclopentane, R113/1-chloropropane, R113/trans-1,2-dichloroethylene, R113/cis-1,2-dichloroethylene, R113/2-chloro-2-methylpropane, methanol, ethanol and isopropanol.

11. The mixture according to Claim 1, which comprises R225cb and at least one member selected from the group consisting of R141, R141b, R141b/dichloromethane, dichloromethane, R122, R132b, R113, R113/R132b, R113/dichloromethane, cyclopentane, 2,2-dimethylbutane, 2-methylpentane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 2,3-dimethylbutane, 2-bromopropane, R113/cyclopentane, R113/1-chloropropane, R113/trans-1,2-dichloroethylene, R113/cis-1,2-dichloroethylene, R113/2-bromopropane, R113/2-chloro-2-methylpropane, methanol, ethanol and isopropanol.

12. The mixture according to Claim 1, which comprises R224ca and at least one member selected from the group consisting of R141b, R141b/dichloromethane, dichloromethane, R122, R132b, R113, R113/R132b, R113/dichloromethane, cyclopentane, 2,2-dimethylbutane, 2-bromopropane, 2-methylpentane, 2,3-dimethylbutane, R113/2 bromopropane, R113/cyclopentane, R113/2,2-dimethylbutane, R113/1-chloropropane, R113/trans-1,2- dichloroethylene, R113/cis-1,2-dichloroethylene, R113/2-chloro-2-methylpropane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, methanol, ethanol and isopropanol.

13. The mixture according to Claim 1, which comprises R225ca, R225cb and at least one member selected from the group consisting of 2-methylpentane, 2,3-dimethylbutane, 2-chloro-2-methylpropane, 1-chloropropane, 2-bromopropane, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, cyclopentane, R122, R141, R132b, R113, dichloromethane, methanol, ethanol and isopropanol.

14. The mixture according to Claim 1, which comprises R225cb, R244ca and at least one member selected from the group consisting of 2,2-dimethylbutane, cyclopentane, 2,3-dimethylbutane, cis-1,2-dichloroethylene, 2-bromopropane, 1-chloropropane, 2-chloro-2-methylpropane, R132b, trans-1,2-dichloroethylene, dichloromethane, R141, R122, methanol and ethanol.

15. The mixture according to Claim 1, which comprises R225ca, R244ca and at least one member selected from the group consisting of 2,2-dimethylbutane, cyclopentane, 2,3-dimethylbutane, dichloromethane, R132b, R141, R122, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 2-bromopropane, 1-chloropropane, 2-chloro-2-methylpropane, methanol and ethanol.

16. The mixture according to Claim 1, which comprises R235ca and at least one member selected from the group consisting of trans-1,2-dichloroethylene, cis-1,2- dichloroethylene, dichloromethane, cyclopentane, 2-bromopropane, 2,2-dimethylbutane, R113, R123, R132b and R141b.

17. The mixture according to Claim 1, which comprises R243cc and at least one member selected from the group consisting of trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 2-bromopropane, 2-methylpentane, dichloromethane, cyclopentane, 2,3-dimethylbutane, R122 and R132b.

18. The mixture according to Claim 1, which comprises R244cb and at least one member selected from the group consisting of dichloromethane, cyclopentane, 2,2-methylbutane, 2,3-dimethylbutane, 2-methylpentane, 2-bromopropane, R122, R132b, R113, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene and R141.

19. The mixture according to Claim 1, which comprises R225ca, R225cb, R244ca and methanol.
20. The mixture according to Claim 1, which comprises R225ca, R225cb, R244ca and ethanol.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 10 2015

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,A	EP-A-0 347 924 (ASAHI GLASS CO., LTD) * Claims 1,2; page 3, lines 19-53; page 4, lines 16-21 *	1-7	C 11 D 7/50 C 23 G 5/028 C 07 C 19/08
A	US-A-3 936 387 (R.E. REUSER) * Claim 1 *	1,5	
A	US-A-3 080 430 (W.V. COHEN) * Claims 1,2; column 2, lines 8-13 *	1,2	
A	FR-A-2 128 555 (IMPERIAL CHEMICAL INDUSTRIES)		
A	US-A-3 476 819 (F.D. TRISHLER)		
A	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 124 (C-580)[3472], 27th March 1989; & JP-A-63 295 699 (DAIKIN LTD) 02-12-1988		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 11 D 7/00
C 23 G 5/00
C 07 C 19/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18-04-1990	TORFS F.M.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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